Final DOE Report

Project Title: Powering Cell Phones with Fuel Cells Running On Renewable Fuels

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Recipient: Tekion
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Working Partners: Tekion
Cost-Sharing Partners: None

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2. Executive Summary

The major goals of this project were as follows:

2.1. Increase the lifetime

At the beginning of the project, some of the materials selected to build the fuel cells were prone to advanced corrosion which translated into rapid degradation even when the cells were operated with dilute formic acid. In the first step accelerated corrosion tests were conducted and components were evaluated for their tolerance to the aggressive nature of formic acid. Test stations were built and the cells were operated for extensive periods of time showing large degradation despite the fact that the corrosion was not an issue anymore. The problem was mitigated by changing the cathode catalyst and also perfecting the cell operating scheme.

2.2. Increase the energy density

To increase the energy density of the cells we increased the concentration of the fuel to 22M (ca. 85 wt%) from 12M (ca. 50 wt%) and we also modified the operating scheme in order to attain the best power density and fuel efficiency with the smallest amount of fuel crossover.

2.3. Lower the material costs

The largest expense of the device is the cathode catalyst. At the beginning of the project Pt loading was over 8 mg/cm^2 on our cathodes. Through optimization work we managed to bring down the cathode loading to approximately half of what we started with.

3. Project Description

3.1. Original project goals and objectives

The original project goals and objectives are as follows:

- Increase the lifetime
- Improve the energy density
- Lower the materials cost

3.2. Variance from original goals and objectives

There has been no change from the original goals and objectives.

3.3. Discussion of work performed

All the tasks that are going to be referred to in the text are associated with the project goals and are presented in Appendix A.

Since formic acid is corrosive, in the first part of the project it was obligatory to determine how components interacted with the aggressive nature of the formic acid. Accelerated corrosion tests were employed for various materials that may be used in our cells and corrosion rates were determined. Examples of such measurements are presented in Figure 1.

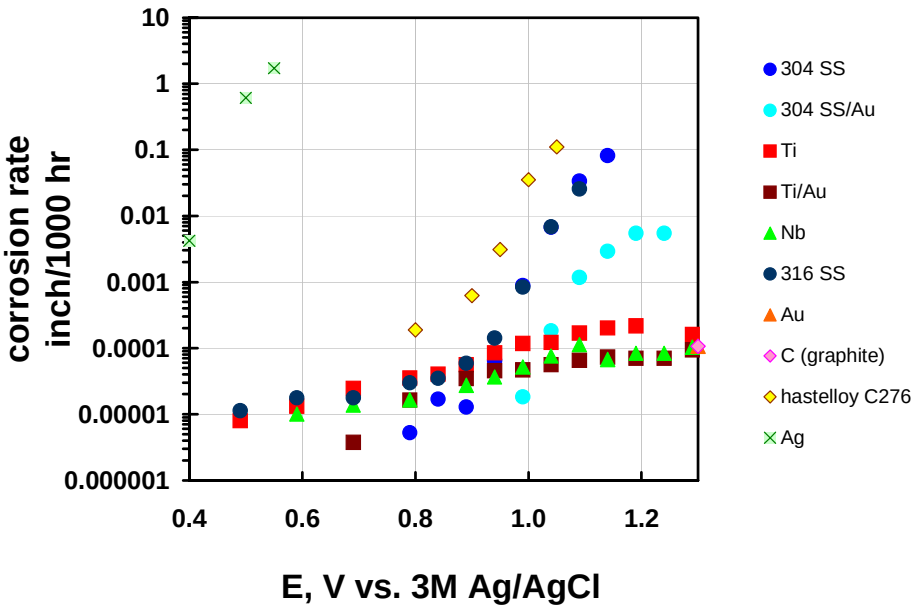

Figure 1. Initial corrosion rates of several metals in 0.5 M sulfuric acid as measured using an electrochemical technique.

Gold (Au) returned satisfying results, so all cell parts were gold plated and they showed good resistance to formic acid (task 1a completed).

Test stations capable of running life tests were built and the life tests commenced (task 1b completed). During the life test fairly large performance decay was noticed as shown in figure 2.

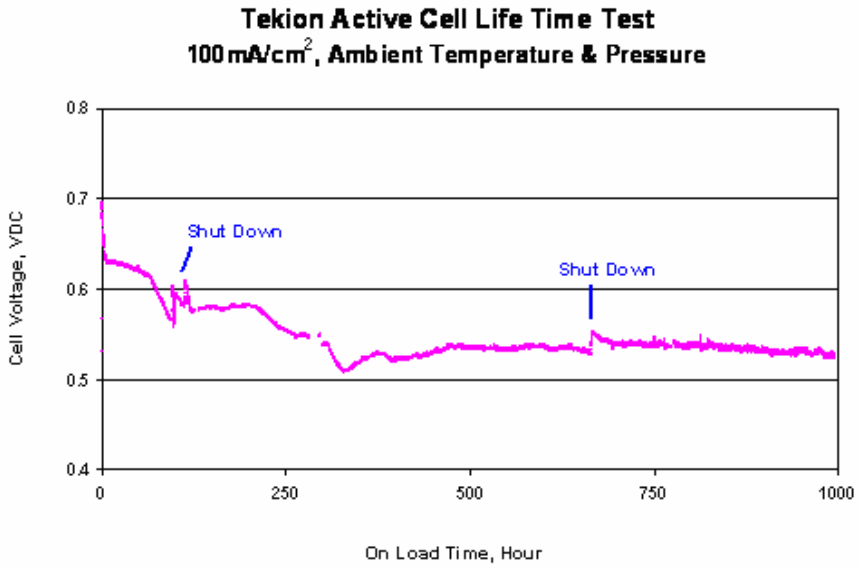

Figure 2. Fuel Cell Performance vs. Life Time at Room Temperature

Although we were able to achieve 1000 hrs of operation (task 1c completed), the decay rate was relatively large. Cell voltage dropped considerably within the first 11 hours, at a rate of ~6.4mV per hour. The degradation rate up to 300 hours is still relatively high compared with 300 hours and beyond. The estimated decay rate was ~0.3mV per hour within the time range of 11 – 300 hours. We have previously observed similar high decay rates at the beginning of the life of the cell. The cell, however, achieved very stable operation after the first 300 hours. The cell voltage subsequently decreased at a much lower rate of only ~0.016mV per hour. The cell resistance started at 75mΩ and increased a little to 87mΩ after 945 hours of operation. This long term test exhibits considerable improvement compared to our previous life time test (the initial 350 hours of a life test, failed after 500 hours due to poor internal contact). It appears the improvements were made by improved cell assembly, namely by making the compression more uniform and cutting the GDLs in a more precise manner (die-cut vs. hand-cut).

In spite of the fact that the cell achieved stable behavior after 300 hours its performance was rather low. Palladium dissolution was then suspected, therefore, experiments were performed to verify whether this was the case.

Liquid samples from anode exhaust were analyzed to determine the Pd catalyst loss during fuel cell operation. The analytical result showed only ppb quantities of Pd, which indicated that if Pd metal dissolution occurs, it does not remain dissolved in the fuel.

Cathode stability was also investigated by evaluating alternative cathode catalysts. The unsupported Pt black was exchanged with a supported catalyst with presumably higher activity. An additional cell was built using the supported catalyst and the life test is presented in figure 3. Unexpected problems with the electronic load unit and power supply occurred near the 2000 hour mark. The problems were corrected and the life test

resumed without delay. The fuel cell appeared to fully recover to the performance that it had before the load unit incident.

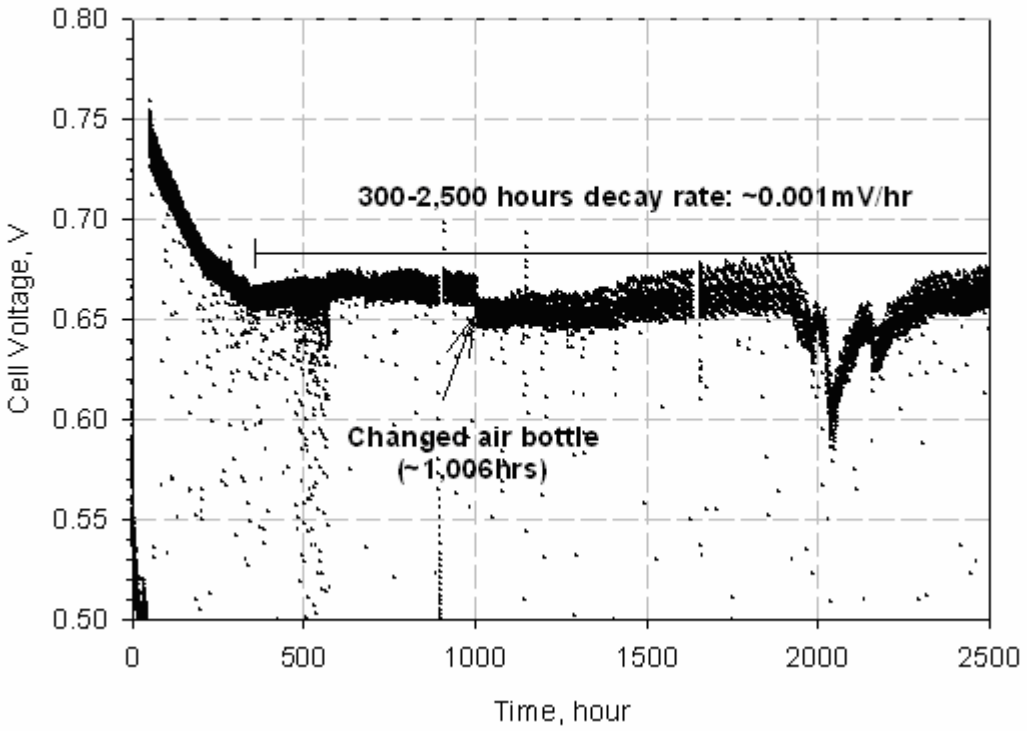

Figure 3. Tekion 5 cm^2 Active Cell Lifetime Test.

(100 mA/cm^2, 40°C, 0.1ml/min 50% FA, 200 sccm dry air, ambient pressure)

The decay rate decreased significantly when compared to the results obtained with the unsupported cathodes (figure 2). High surface area supported catalysts on the cathode side of the formic acid fuel cell demonstrated a dramatic improvement in the performance and especially in the stability of the fuel cell under operating conditions. This is presumably a result of the significant increase in dispersion that the supported catalyst has compared to the unsupported catalyst. Improved catalyst dispersion within the catalyst layer can reduce agglomeration of the cathode catalyst particles which would decrease the electrochemical active area of the cathode. Therefore, stability of the cathode is dramatically improved.

To increase energy density, it was necessary to operate the formic acid fuel cell with higher concentrations of formic acid. The preliminary tests using 20M formic acid showed ca. 0.7V at 100 mA/cm^2 during the first hour, after which the performance decreased to about 0.6V at the end of the second hour. At the end of an 8 hour testing period the performance stabilized around 0.5V. This was likely due to severe crossover at elevated concentrations and/or dehydration of the membrane, which could occur when

Nafion® is in contact with a hygroscopic medium such as highly concentrated formic acid (task 2a completed).

Up until this point, all the experiments were performed in active cells. This means that there was continuous and forced flow of formic acid and air through the anode and cathode, respectively. Unfortunately, active cells are not a viable solution for potential systems based on formic acid fuel cell technology due to issues related to crossover and the necessity of air fans which cause significant parasitic losses. Moreover, a continuous flow of formic acid would necessitate the addition of a recirculation loop for the unreacted fuel leaving the anode, which, in turn complicates the balance of plant.

In order to address these problems we designed a new fuel delivery system for formic acid, which reduced the exposure of the membrane to the high concentration formic acid. We also changed our cell design radically to passive (self breathing) cathode cells (Task 2c completed). These passive cells were developed entirely at Tekion for portable applications. This change is a prerequisite for a cell that will be integrated in a product. These modifications had a very positive impact on cell performance and fuel utilization (Task 2b completed). This change enabled the increase in formic acid concentration from 12M to 22M which is the flammable limit at which formic acid can be carried on public transportation. Since fresh, concentrated acid is administered at a very controlled manner the evaporative losses are nearly eliminated (task 2d completed). An example of a life test is presented in figure 4.

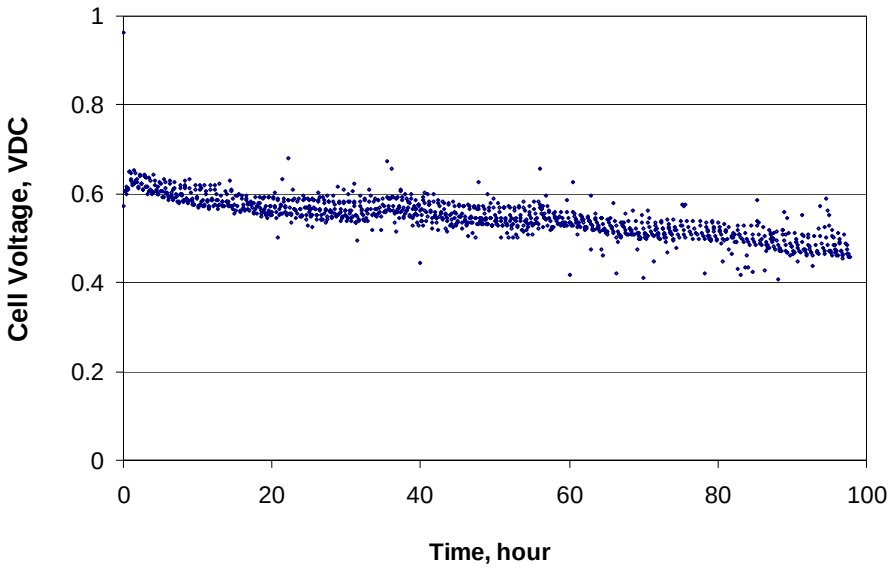

Figure 4. Life Test on a Passive Cell Operated at 100mA/cm^2 with 22M acid

The operating scheme also enabled us to redesign the acid reservoir. Since no exhaust is returned to the cell the acid reservoir has a very simple construction that enables for rapid swap of cartridges (task 2c completed).

The last goal of this project was to decrease the cost of the materials used in manufacturing these cells. We have already identified that the most expensive component was the cathode catalyst and thus we attempted to decrease its loading.

At the beginning of the project, we investigated the possibility of operating the fuel cells with cathode loadings of less than 1 mg/cm^2 and the results are presented in figure 6.

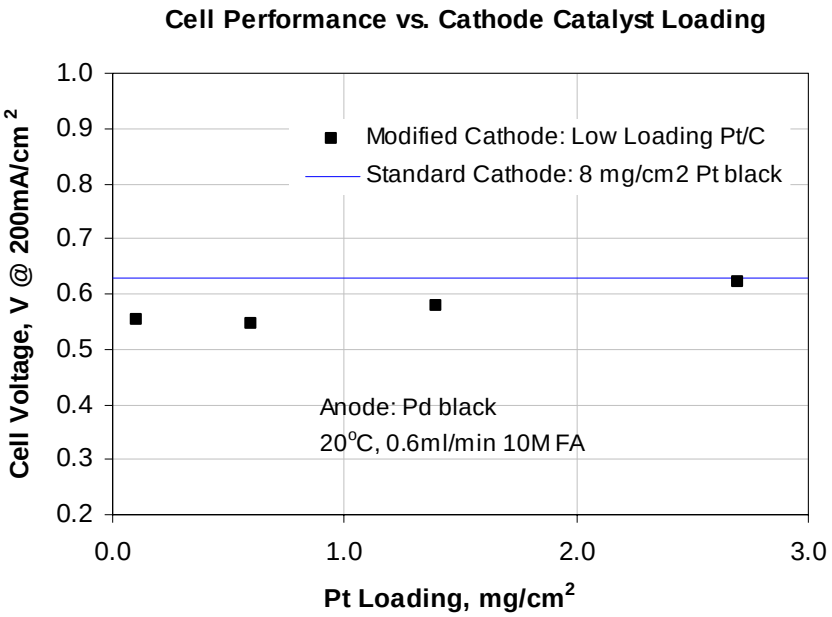

Figure 6. Effect of Pt loading on performance at 20°C

The low loading cathodes delivered fairly good performance, almost as good as the standard high loading electrodes but these experiments were carried out in active cells and with low concentration formic acid (10M).

It was necessary to determine what the impact was of lowering the cathode loading on the performance of passive cells operated with 22M formic acid. To accomplish this task, Tekion has designed a matrix of experiments that studies the influence of catalyst loading and electrode ionomer content on the performance of the passive formic acid fuel cell.

The goal was to determine the optimum cathode catalyst loading and Nafion® ionomer content. The experiments were carried out at several current densities to cover the entire range of possible operating points. The cell voltages at each current density were measured.

Tekion fitted the responses using an empirical quadratic model and the model equation is:

$$E_{Average} = a + b \cdot CL + c \cdot NC + d \cdot CL \times NC + e \cdot CL^2 + f \cdot NC^2$$

Where:

$E_{Average}$ = average cell voltage (V)
a, b, c, d, e, f = model coefficients
CL = cathode loading (mg/cm^2)
NC = Nafion® content (% wt)

The expanded matrix of experiments, the corresponding values of the responses, the model responses and the correlation between experiment and model calculated values were as follows:

Table 1. Matrix of MEAs for the Cathode Loading – Nafion® Ionomer Content Study

Cathode Loading	Nafion Content	100 mA/cm2			120 mA/cm2			150 mA/cm2			175 mA/cm2		
		Experiment	Model	%Error	Experiment	Model	%Error	Experiment	Model	%Error	Experiment	Model	%Error
5.46	30	0.6393	0.6428	-0.5%	0.5934	0.6006	-1.2%	0.5322	0.5460	-2.6%	0.4587	0.4955	-8.0%
4.51	20	0.6363	0.6250	1.8%	0.5983	0.5888	1.6%	0.5538	0.5440	1.8%	0.5181	0.5048	2.6%
5.84	20	0.6235	0.6335	-1.6%	0.5842	0.5885	-0.7%	0.5276	0.5440	-3.1%	0.4788	0.5068	-5.8%
5.27	26.6	0.6368	0.6478	-1.7%	0.5940	0.6051	-1.9%	0.5414	0.5560	-2.7%	0.4946	0.5096	-3.0%
4.66	25	0.6453	0.6446	0.1%	0.6069	0.6045	0.4%	0.5573	0.5580	-0.1%	0.5059	0.5124	-1.3%
6.16	26.6	0.6367	0.6489	-1.9%	0.6005	0.6031	-0.4%	0.5565	0.5540	0.4%	0.5173	0.5086	1.7%
4.216	30	0.6579	0.6420	2.4%	0.6147	0.6020	2.1%	0.5660	0.5480	3.2%	0.5210	0.4973	4.5%
6.027	23.3	0.6639	0.6461	2.7%	0.6010	0.5998	0.2%	0.5630	0.5540	1.6%	0.5293	0.5128	3.1%
6.074	30	0.6598	0.6422	2.7%	0.6133	0.5988	2.4%	0.5596	0.5440	2.8%	0.5175	0.4941	4.5%
4.306	20	0.6308	0.6235	1.2%	0.5940	0.5886	0.9%	0.5589	0.5440	2.7%	0.5176	0.5043	2.6%
5.39	20	0.6189	0.6310	-2.0%	0.5817	0.5890	-1.3%	0.5371	0.5440	-1.3%	0.5056	0.5063	-0.1%
1.72	30	0.6282	0.6322	-0.6%	0.5922	0.5962	-0.7%	0.5429	0.5450	-0.4%	0.4921	0.4965	-0.9%
4.08	28	0.6404	0.6443	-0.6%	0.6070	0.6051	0.3%	0.5549	0.5550	0.0%	0.5074	0.5060	0.3%
2.92	30	0.6309	0.6383	-1.2%	0.6008	0.6004	0.1%	0.5477	0.5480	-0.1%	0.4996	0.4977	0.4%
1.72	25	0.6222	0.6250	-0.5%	0.5903	0.5967	-1.1%	0.5419	0.5530	-2.0%	0.4972	0.5072	-2.0%
6.57	35	0.6125	0.6127	0.0%	0.5786	0.5744	0.7%	0.5126	0.5080	0.9%	0.4545	0.4510	0.8%
2.34	35	0.6327	0.6205	1.9%	0.5914	0.5795	2.0%	0.5287	0.5150	2.6%	0.4757	0.4627	2.7%
4.397	35	0.6053	0.6206	-2.5%	0.5603	0.5811	-3.7%	0.4918	0.5150	-4.7%	0.4407	0.4592	-4.2%
4.33	27.5	0.6343	0.6452	-1.7%	0.5858	0.6055	-3.4%	0.5277	0.5560	-5.4%	0.4916	0.5076	-3.3%

As shown by Table 1, Tekion tested MEAs with catalyst loadings ranging from 1.72 to 6.57 mg/cm^2 and with Nafion® content ranging from 20 to 35%$_{wt}$. The average cell voltages at 100, 120, 150 and 175mA/cm^2 are illustrated in the table. The calculated values using the above model and the correlation between the experimental and calculated values are also shown. It can be easily noticed that the correlation is excellent with almost all values falling within a 5% error.

At each of the 4 current densities, an optimum point was determined. In order to validate the model, Tekion prepared one MEA corresponding to the optimum point at 120mA/cm^2. The optimum catalyst loading and Nafion® content at 120mA/cm^2 are 4.4mg/cm^2 and 27.5%, respectively. Therefore, Tekion prepared an MEA with catalyst loading of 4.33 mg/cm^2 and 27.5% Nafion® ionomer content. Figure 7 plots the optimum points at each current density (red diamonds). Also, the result obtained with the MEA is also shown in the plot (magenta square).

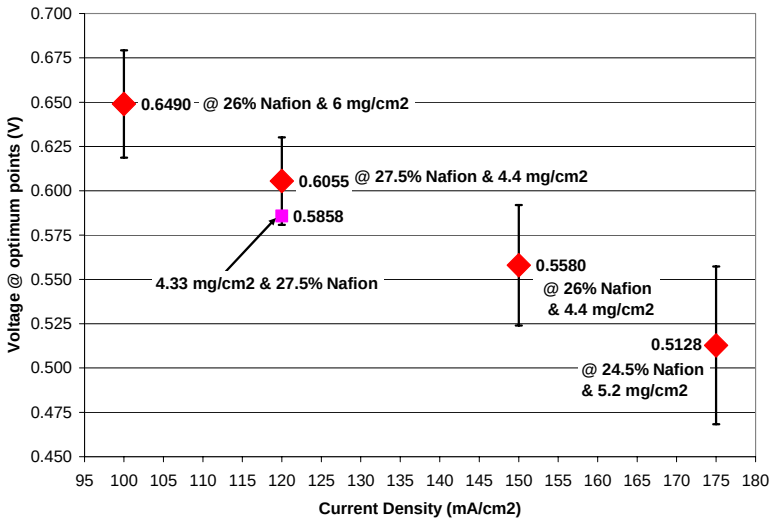

Figure 7. Optimum cathode loading and Nafion® content and the voltage response at 100, 120, 150 & 175mA/cm^2.

At the beginning of this project, Tekion's standard cathode loading was on the order of 8 mg/cm^2. Through optimization work, Tekion has been able to lower the loading to nearly half, thus achieving the goal of Task 3.

3.4. Conclusions and future work

Over the course of this project we have accomplished all of the goals that were set in the proposal and all the tasks associated with these goals were entirely and successfully achieved.

We started with standard research-type active cells and successfully developed novel passive cells designed specifically to address issues related to maximizing fuel efficiency including anode degradation, fuel crossover through the membrane, operation with very high concentration formic acid, all with air-breathing cathodes to minimize parasitic losses. Ultimately we were able to put cells together in a stack and continuously operate them for more than 600 hrs with minimal decay, proving therefore that the technology can be feasible for implementation in portable devices.

Appendix A – Task Schedule

Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1a	Initial corrosion rates measured	12/31/04		1/8/05	100%	Found materials that resist formic acid
1b	Setup 1000 hr testing	1/20/05	02/5/05	03/05/05	100%	Completed
1c	1000 hr runs	09/30/05		9/30/2005	100%	2,500 hrs completed
2a	Identify performance limitations at higher concentrations	3/31/05	03/1/05	4/07/05	100%	Found loss of activity and loss of electrical contact
2b	Reduce performance limitations by 50%	09/30/05		06/01/05	100%	Improved operating scheme allows good performance and stability
2c	Redesign Reservoir	12/31/05		06/01/06	100%	Unit cell design improved anode reservoir for fuel delivery
2d	Reduce evaporative losses by 90%	09/03/06		08/01/06	100%	The evaporative losses are almost non-existent due to the new operating scheme
3	Reduce cathode catalyst loading	09/03/06		08/15/06	100%	Cathode loading was lowered to less than half of that from when the project commenced

Appendix B – Final Spending Schedule

Final Spending Schedule

Project Period: 09/30/04 to 09/30/06

Task	Approved Budget	Final Project Expenditures
Task 1 Long Term Testing	$109,375	$109,375
Task 2 Raising Specific Power	$91,404	$91,404
Task 3 Cost Reduction	$49,221	$49,221
Total	$250,000	$250,000
DOE Share	$250,000	$250,000
Cost Share	N/A	N/A

Appendix D – Energy Savings

There are also important energy savings with Tekion's formic acid fuel cells. Presently, there are 165,653,238 phones in the United States. Each uses about 9 kW-hr of electricity per year for recharge, for a total energy utilization of 1.5×10^{9} kW-hr/year or 5×10^{12} btu/year. While this is a small fraction of the total US electricity generation for 2001 (3.8×10^{12} kW-hr/year), if Tekion can find a way to save 1×10^{9} kW-hr/year, it will be a significant number. After all, even after years of investment, wind power generates only 5×10^{9} kW-hr/year and photovoltaics generate only 4×10^{8} kW-hr/year. Tekion's design replaces electricity generated from coal or nuclear with formic acid, a fuel that can be generated from renewable resources. The efficiency can be as high as 50%. This is high when compared to battery chargers. Thus, there could be a significant immediate savings with Tekion technology and the possibility of long-term advantages.

Table A compares the energy that would be needed in various scenarios. There are presently 165,653,238 phones in the US and approximately 800,000,000 worldwide. Each phone needs 9 kw-hr/yr or a total of $1.5x10^{9}$ kw-hr in the US or $7.2x10^{9}$ kW-hr world wide. Price-Waterhouse-Coopers projects that 50% of cell phones will be powered by fuel cells by 2011. Those phones require $7.5x10^{8}$ kw-hr of electricity to operate. If the phones run on batteries, then the power system will need to burn $7.5x10^{8}$ kw-hr/0.55/0.95/0.4 =$3.4x10^{9}$ kw-hr of fossil fuel to produce the electricity, where 0.55 is the generator efficiency, 0.95 is the power transmission efficiency and 0.4 is the battery charger efficiency. In contrast, the cell phones will not require any fossil fuels, if the phones are powered with formic acid made from renewable sources. If the formic acid is made form oil, $1.5x10^{9}$ kw-hr will be needed, assuming the fuel cell runs at 0.7 V with 85% fuel utilization efficiency. So there is the opportunity to save energy with our devices.

Table A: Comparison of the fossil fuel needed in various scenarios

Type of Device	United States	World
#phones using fuel cells	80,000,000	400,000,000
Energy used by phones	$7.5x10^{8}$ kw-hr	$3.6x10^{9}$ kW-hr
Fossil fuel needed if the cell phones run on batteries	3.4×10^{9} kw-hr	1.7×10^{10} kw-hr
Fossil fuel needed if the cell phones run on Formic Acid Fuel Cells where the formic acid is made from renewable sources	0	0
Fossil fuel needed if the cell phones run on Formic Acid Fuel Cells where the formic acid is made from oil	$1.5x\ 10^{9}$ kw-hr	8×10^{9} kw-hr